III.B.7. Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity (New FY 2004 Project)

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Objectives

- Develop a reversible, 7.5 hydrogen wt.% capacity complex hydride with the kinetics required for automotive PEM fuel cell operation, which can be cyclically discharged and recharged for 500 cycles.
- Prepare such a storage media in sufficient quantities to enable evaluation in a subscale hydrogen storage system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Weight and Volume
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

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Approach

The goal of the project is to develop a new complex hydride compound capable of reversibly storing hydrogen with capacity greater than 7.5 wt.% for 500 regeneration cycles with 100% efficiency. The project will develop, prepare and deliver such a storage media in sufficient quantities to enable evaluation in a sub-scale hydrogen storage system being developed under the DOE contract "High Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Based Complex Compound Hydrides."

The objective of this project is to discover new reversible high hydrogen content complex hydride compounds of the structure $Na_yM_{+ix}(AlH_4)_{y+ix}$, in the quaternary phase space between sodium hydride (NaH), alane (AlH_3), transition metal or rare earth (M) hydrides (MH_z, where z= 1-3) and molecular hydrogen (H_2). This project will encompass all of the technology development stages for identifying, developing and commercializing complex hydride compound hydrogen storage media to meet the DOE technical targets. The team will accelerate the discovery of new complex hydride compounds and guide experimentation with first principles modeling. Simultaneously, the team will apply multiple synthetic methodologies to isolate new hydrides, and couple thermodynamic predictions and structural characterizations to verify structures of newly identified phases. The team will conduct three levels of performance evaluations to select compositions for further development, optimize dehydrogenation and hydrogenation catalysis with spectroscopic mechanistic studies and first-principles screening simulations, develop manufacturing processes to reduce cost and scale-up production, and develop business analyses for the commercialization of hydrogen storage systems integrated with fuel cell power plants.

The following tasks are planned for year 1.

Task 1.0 First Principles Modeling

- Predict new quaternary complex hydride compositions to recommend for synthesis targets
- Evaluate the theoretical phase stability and reversible hydrogen content of the best quaternary complex hydride candidates, and identify new catalyzed quaternary compositions with decreased dehydrogenation activation barriers.
- The compilation of a candidate structure list for ground state screening simulations from the structural and thermodynamic parameters of analogous compounds will be completed.
- Present compositional section phase diagrams and pressure-composition-temperature diagrams established to evaluate the phase stability and reversible hydrogen content of high capacity systems

Task 2.0 Synthesis

- Materials will be synthesized via three distinct processing routes: solid state processing, molten-state processing and solute based processing. Synthesis attempts will be performed on lithium and titanium alanate compounds and mixed sodium/lithium/titanium compounds. Following identification and synthesis of such phases, 5-10 g samples will be synthesized for performance evaluations.
- Synthesis attempts will be performed on compounds and mixed sodium compounds, which are hypothesized to exist based on high catalytic activity and solubility in $NaAlH_4$
- Initial samples will be analyzed and processing iterated to synthesize 5-10 g samples for performance evaluation.
- Analyses will yield data on the temperature and preliminary thermal properties of dehydrogenation reactions

Task 3.0 Analysis

- Thermodynamic variables will be determined for a selected number of compounds, which hold promise for enhanced hydrogen storage capability. This information will be used for ab-initio model verification.
- Once a new phase has been identified and a process developed to synthesize it in reasonable purity, it will be tested using a Sievert's apparatus specifically designed to measure solid/gas reaction kinetics. Each sample will be prepared identically to yield a comparative base between current state-of-the-art $NaAlH_4$ compounds under development and the new high hydrogen capacity materials being developed in this project.
- Thermodynamic variables will be determined for a selected number of compounds, which hold promise for enhanced hydrogen storage capability. This information will be used for ab-initio model verification.

Task 4.0 Performance

- Measure solid/gas reaction kinetics; confirm capacity